U.S. ARMY ARMAMENT, RESEARCH, DEVELOPMENT, & ENGINEERING CENTER

Nanopowder Synthesis & Associated Safety Precautions at ARDEC: Partnering with NIOSH

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

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Outline of Talk

- Relevance of Nanomaterials & Technology
- Why Nano?
- Nano Prototyping Facility
- Nanomaterial Synthesis
- Serving as a NIOSH “Test Bed”
- Test Bed Findings
- Best practice recommendations

Powders, powders, powders…

The US Army is developing anew materials for both armor and anti-armor applications. There is a strong emphasis on _powder technologies_ since powders are an integral part of the Army mission.

Explosives (e.g., RDX)

Propellants (e.g., Black Powder)

Relevance of Particulate Technology

Particulate materials and processing technologies are highly relevant to our mission at ARDEC

- Most energetic materials use particulate precursors
- Materials of choice for warheads are refractory metals (e.g. molybdenum and tantalum), which depend on particulate processing technology
- Alternate materials for kinetic energy penetrators (tungsten) can only be processed via particulate technology
- Advanced ceramics for armor require particulate materials and technology
- Surface modifications, protection, and functional coatings also utilize powders and particulate technology
- Ultra-light weight and high specific strength armament components depend on particulate materials

Nanotechnology is a natural extension of particulate technology

Why Nano?

Where's the motivation?

If you were in a hurry to get out the door and needed some sugar in your coffee, which do you choose?

Sugar Cubes

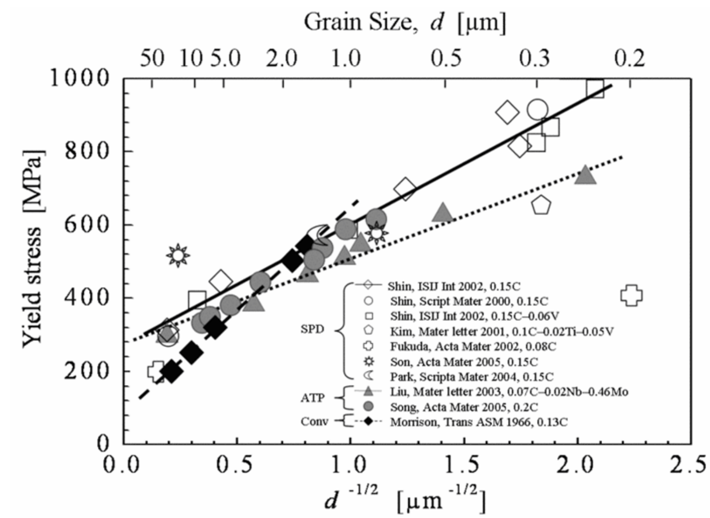
Confectioners Sugar

It's all about <u>surface area</u>, more atoms at the surface.

Why Nano?

What material properties can nanomaterials affect?

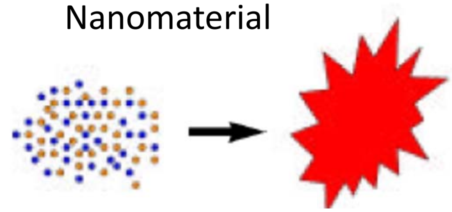
- Mechanical
  - Strength - Smaller grain size → stronger materials
    - ➢ Lightweight materials & composites
    - ➢ Increased survivability
  - Toughness
    - ➢ Nanocomposite materials
- Chemical
  - Increased reactivity due to surface area
    - ➢ Higher energy release rates
    - ➢ Superior burn rates
    - ➢ Tunability
- Electrical, Optical, Magnetic…etc.



Conventional Material

- mass transport an issue
- lower power
- energy lower (incomplete reaction)

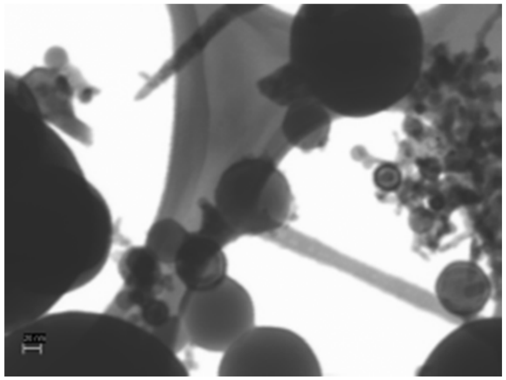
Nanomaterial



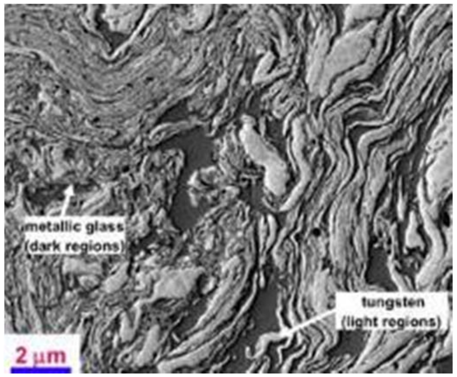
- mass transport minimized
- higher power (faster reaction)
- higher total energy

Defining "Nanomaterial"

- Nanomaterial – A material having at least one dimension in the 1 – 100 nm size range
  - Nanophase material – This consists of materials where the primary particle size is nanoscale
  - Nanostructured material – Materials which are not necessarily nanoscale, but possess features (e.g., grain size) which are nanoscale

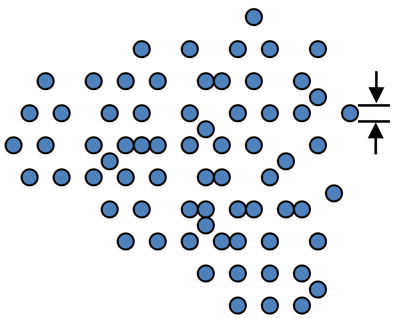


Nanophase powder



Nanostructured material

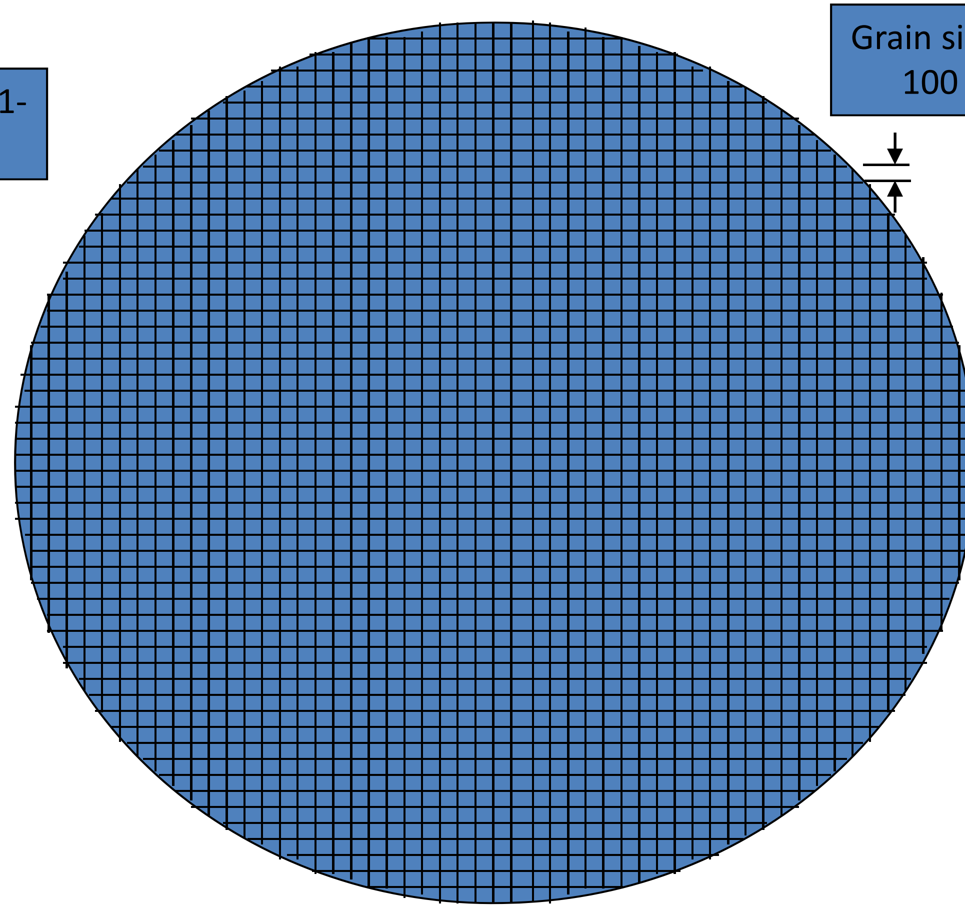
Nanopowder



Particle size is 1-100 nm

Nano-*structured* Powder

Grain size is 1-100 nm

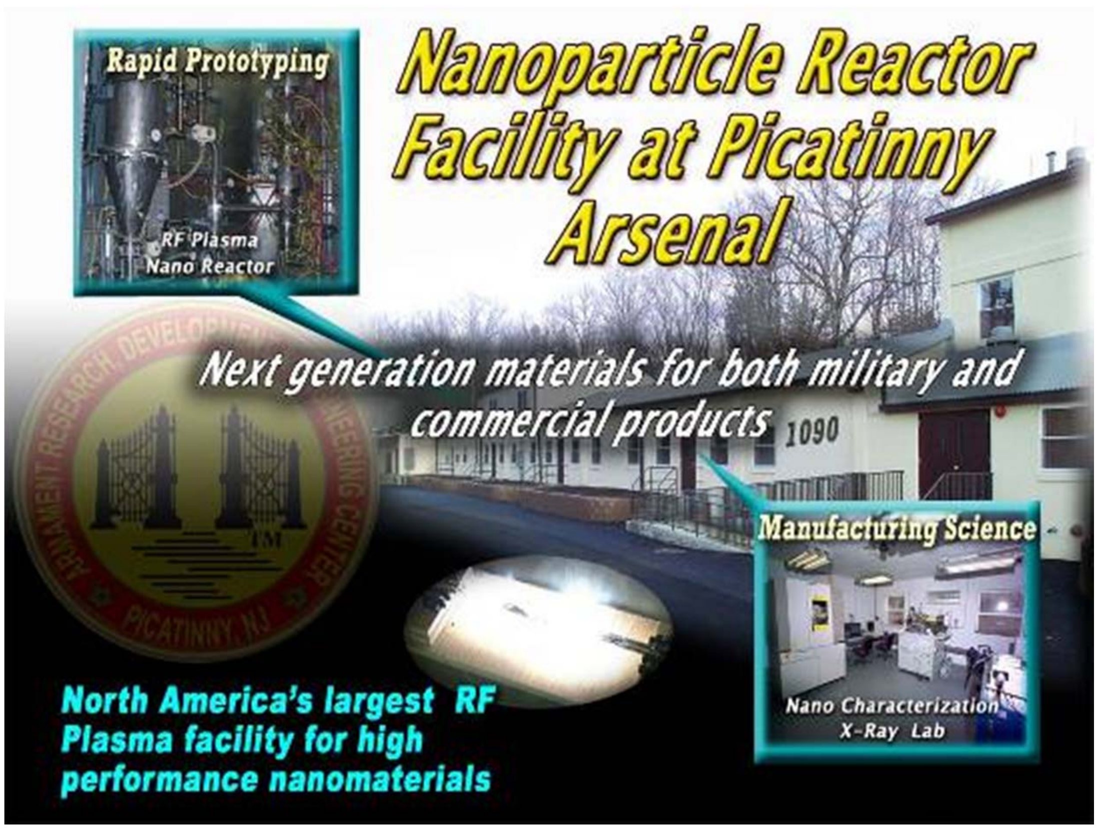


ESOH best practices still being developed

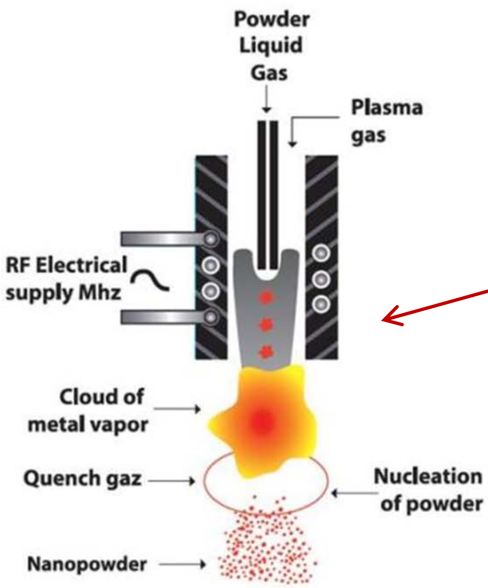
As safe as conventional materials

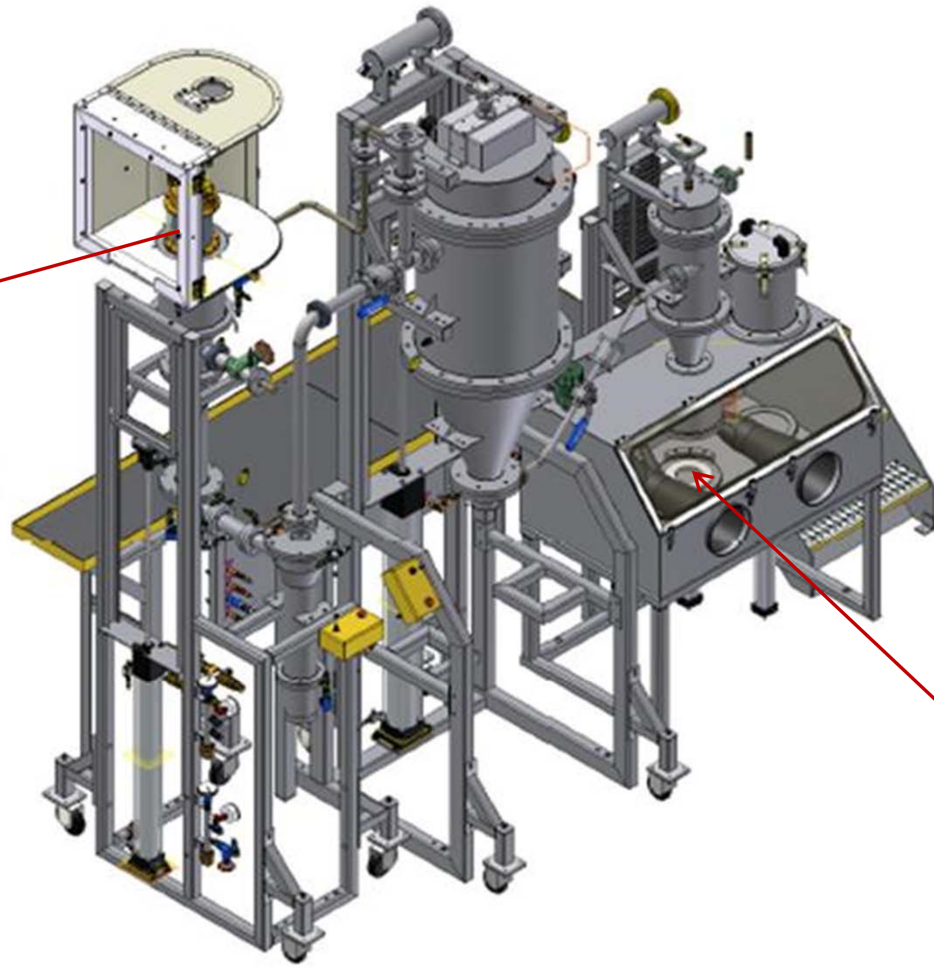
Nano Prototyping Facility

An integrated state-of-the-art facility to synthesize, process, and characterize nanophase and nanostructured materials, fully dense near-net shape bulk components, and nanostructured coatings.

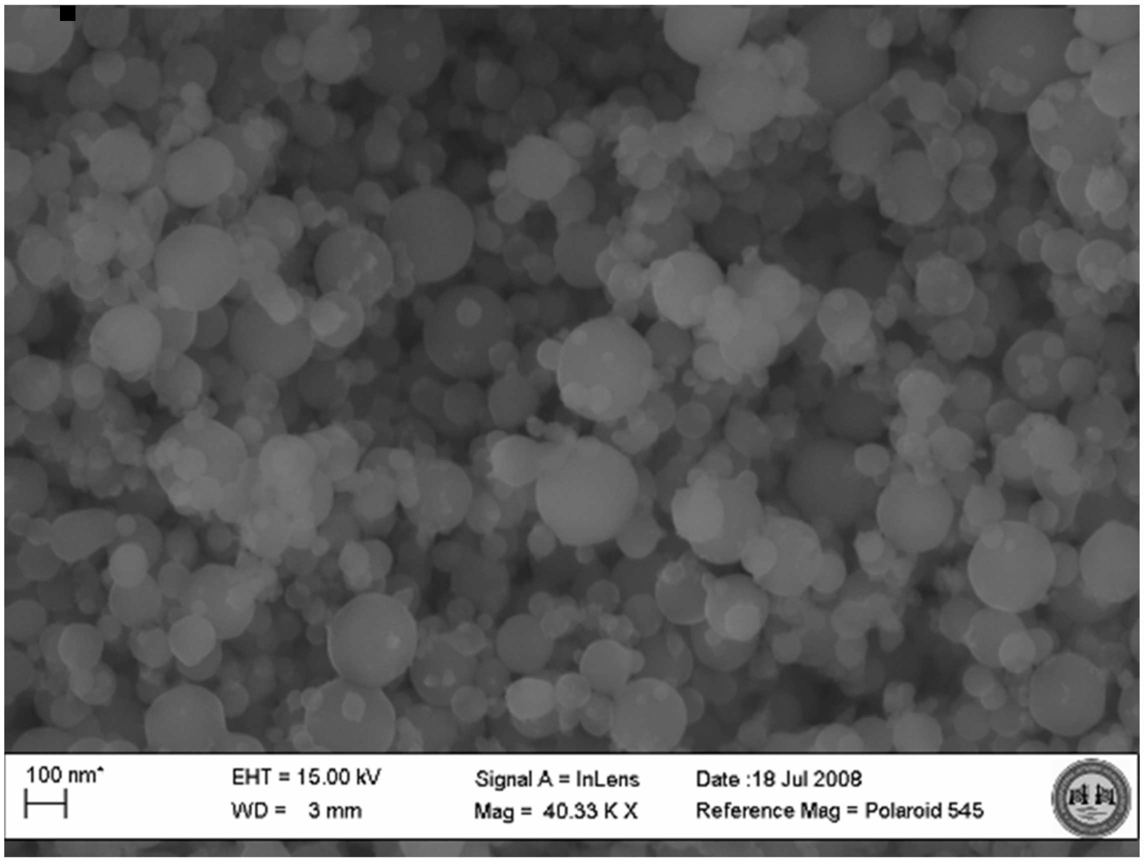


Slide taken from General Griffin's "Avenues of Change" Brief, Jul 2007


Powder
Liquid
Gas
Plasma
gas
RF Electrical
supply Mhz
Cloud of
metal vapor
Quench gaz
Nucleation
of powder
Nanopowder



Nano Aluminum



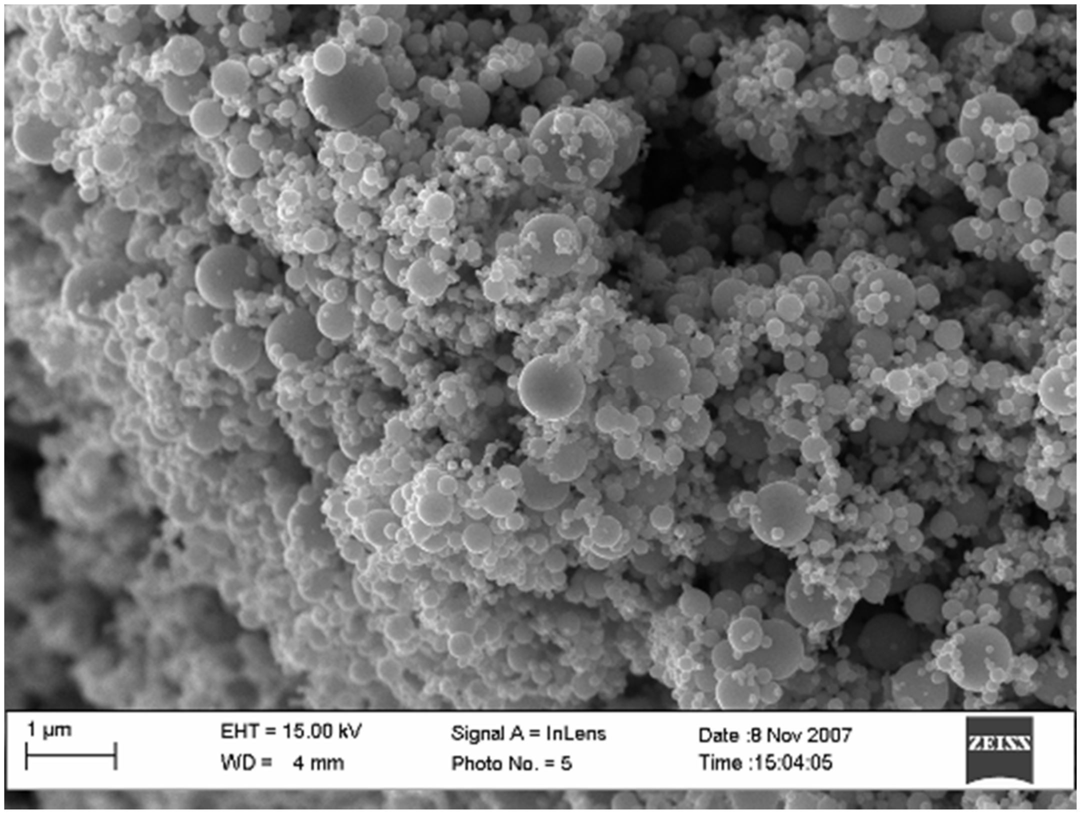
Applications:

✓Propellants

✓Energetics

- Primers
- Explosives
- Pyrotechnics

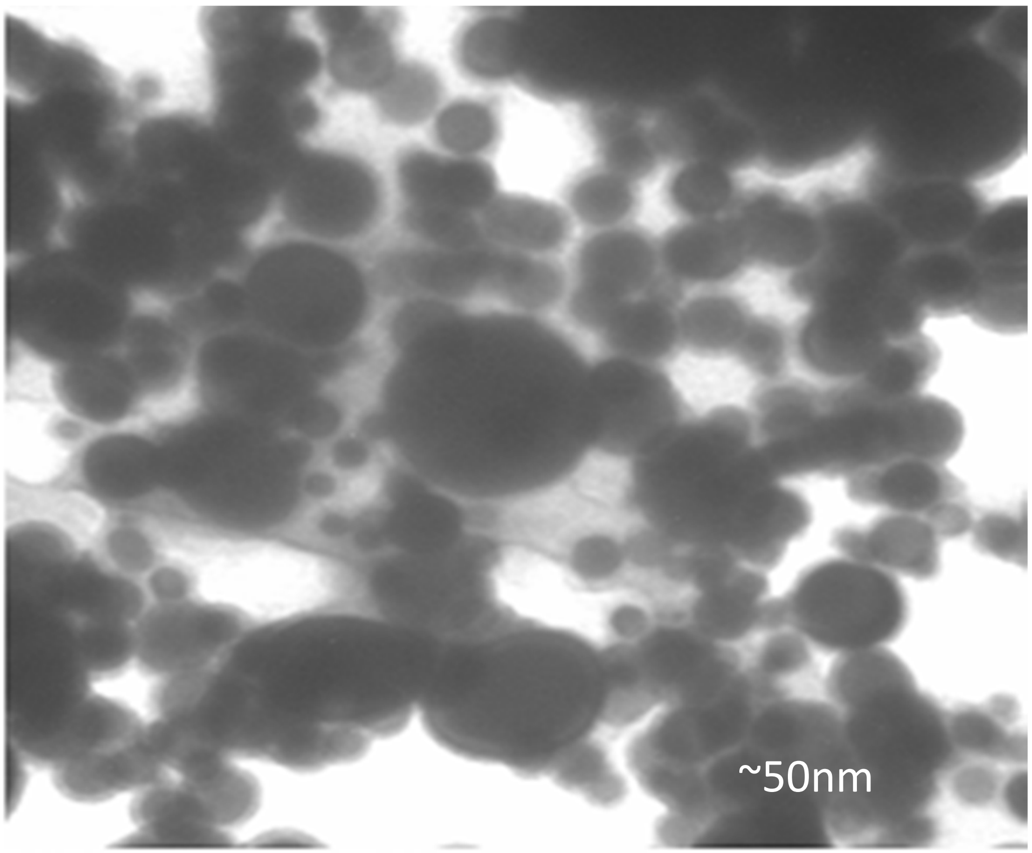
Nano Iron



Applications:

Primarily developed for **PM-CCS** as a second source for specialty Infrared materials for the **M211 Countermeasure Decoy**, but will also play a role in Tunable Pyrotechnics program

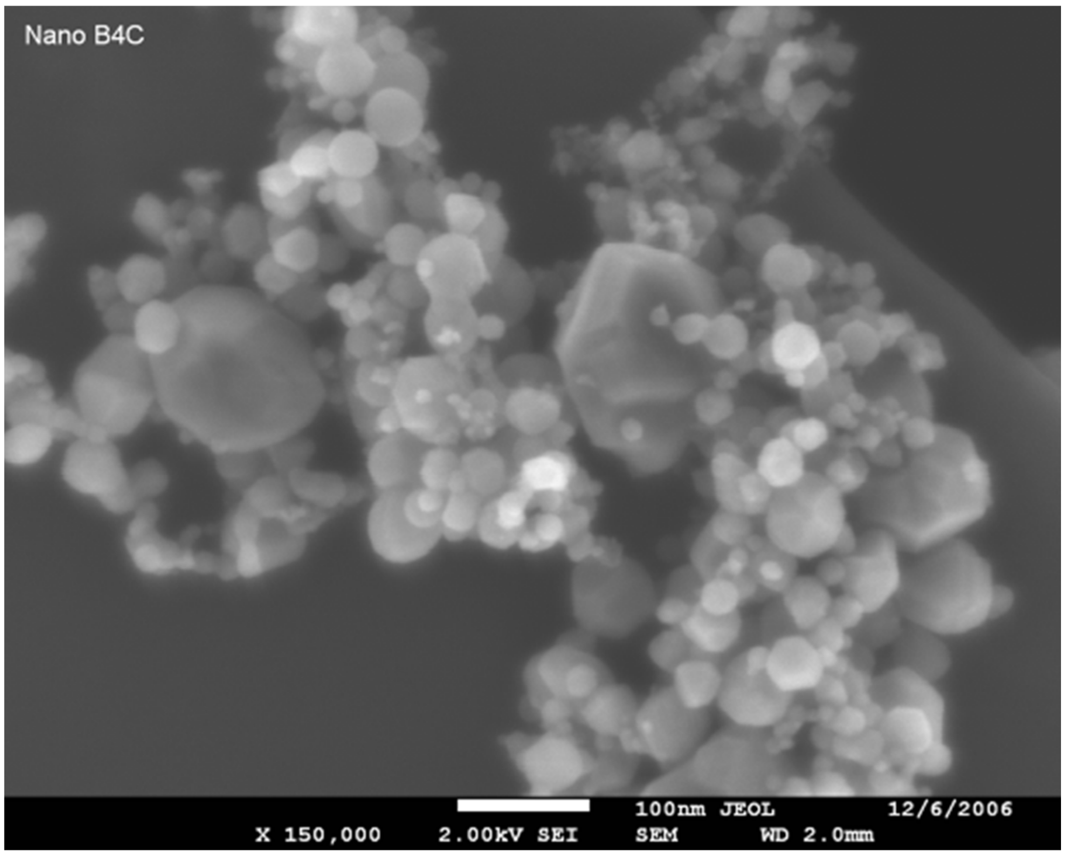
Nano Tungsten (MMA Coated)



Applications:

Primarily being developed as a replacement for Depleted Uranium (DU) in Kinetic Energy (KE) Penetrators.

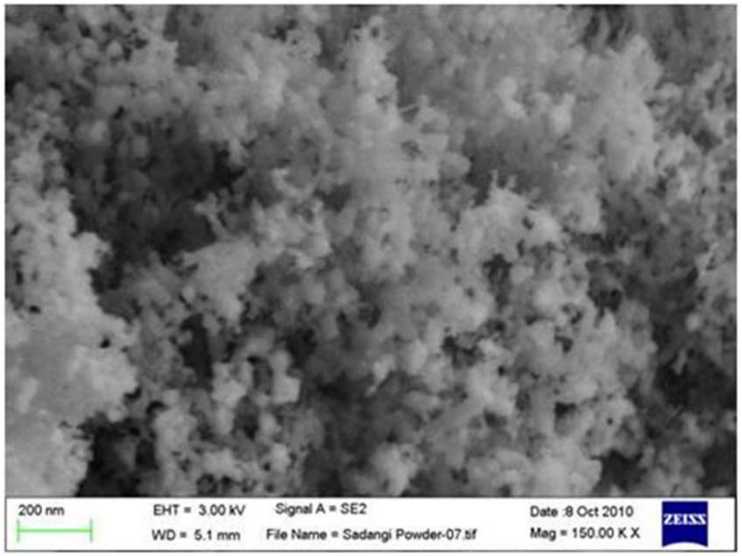
Nano B_4C

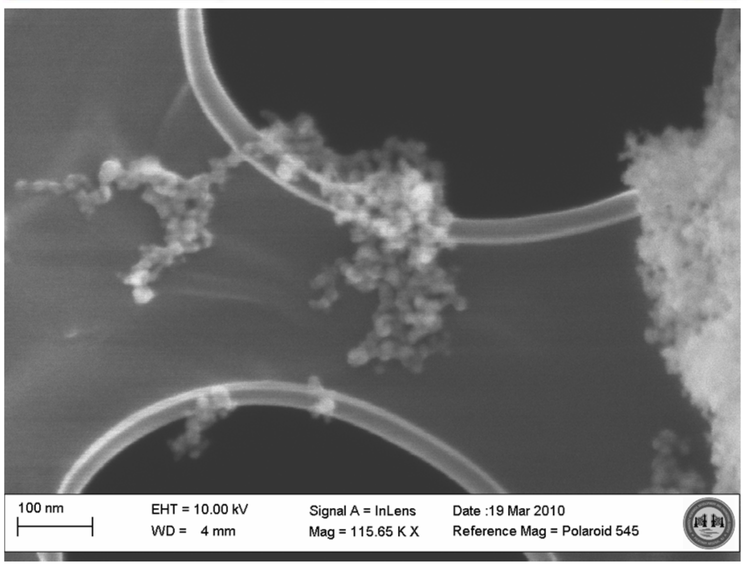


Applications:

Boron Carbide (B_4C) is a conventional armor material. Nano B_4C has the potential for increased toughness. This can increase survivability and/or decrease weight by requiring less material.

Nano Mixed Oxides





Applications:

Mixed-oxide nanomaterials are of interest for a myriad of applications including optical materials, catalysts, magnets and piezoelectrics to name a few.

NIOSH Test Bed

Timeline:

- **Sept 2006**? – ARDEC Volunteered to serve as a "Test Bed" for NIOSH's Nanotechnology Field Research Team – Dr. Mark Methner
- **March 2007** – Initial visit (baseline sampling)
- **May 2008** – Follow-on visit (sampling/characterization)

Test Bed Concept: Allow NIOSH Field Research Team full access to facility in order to assess current ESOH practices and make recommendations for best practices to improve worker health and safety.

What Site Visits Entailed: NIOSH personnel conducted particle sampling of both open areas and personal breathing zone (PBZ) under various conditions. Also performed characterization on particles

Established* Best Practices

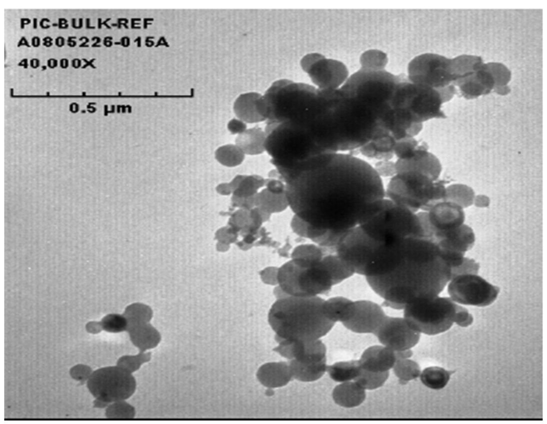
- All workers utilize nitrile gloves when dealing with nanopowders
- All powders handled in a fume hood unless in a solvent/solution
- Clean-up of any residual powders should be done wet using either water or approved cleaning solvents (e.g. Simple Green)
- Clean-up of reactor systems done using explosion-proof, submerged recovery (water-based) vacuum cleaner (Vac-U-Max, Belleville, NJ)
- Full-body Tyvek™ suit with hood, nitrile gloves, and a NIOSH-approved, powered air purifying respirator (PAPR) or supplied air hood (Mine Safety Appliance [MSA] Corporation, Pittsburgh, PA).

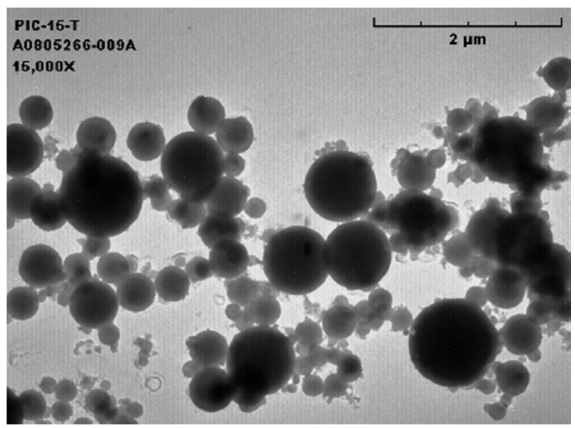
Images taken from www.msanorthamerica.com

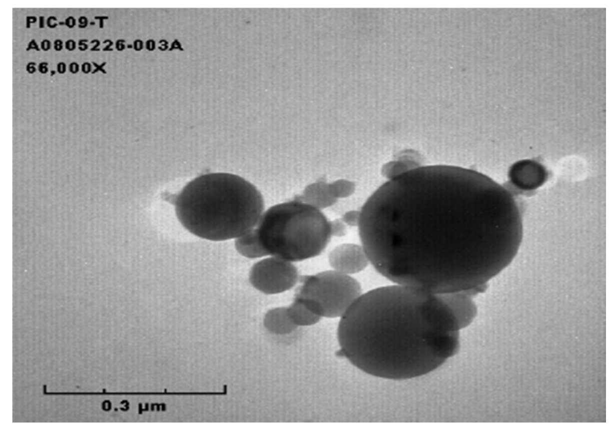
*Best practices conducted prior to NIOSH test bed activities

Findings

Sample location/operation	Sample type	Aluminum concentration (μg/m³) Ventilation On	Aluminum concentration (μg/m³) Ventilation Off
Plasma torch reactor chamber during cleaning/brushdown	AS	89	40
	PBZ	232	157
Filter chamber during cleaning/brushdown	AS	20	276
	PBZ	100	-- [a]
Cyclone cleanout/brushdown	AS	27	246
	PBZ	13	-- [a]
Glovebox cleanout	AS	1317	-- [a]
	PBZ	868	-- [a]
	PBZ	840	-- [a]







Transmission Electron Microscopy (TEM) images of particles collected on sampling filters

AS – At Source
PBZ – Personal Breathing Zone

Findings

ample location/operation	Particle size (nm)	Measured Concentration **Ventilation Off**	Average Background Concentration	Adjusted * Concentration **Ventilation Off**	Measured Concentration **Ventilation On**	Average Background Concentration	Adjusted * Concentration **Ventilation On**
orch reactor chamber cleanout	300	113,636 [a]	35,164	78,472 [s]	98,180 [a]	42,473	55,707
	500	73,538 [a]	2,476	71,062 [s]	3,857	2,086	1,771
	1,000	56,902	419	56,483	643	378	265
	3,000	42,081	92	41,989	136	89	47
	5,000	34,414	9	34,405	28	2	26
	10,000	33,226	5	33,221	26	1	25
	(10 - 1000)	9,348	2,656	6,692	>100,000 [b]	11,786	88,214
ilter chamber cleanout	300	86,953 [a]	35,164	51,789	52,957	42,473	10,484
	500	47,854	2,476	45,378	2,063	2,086	0
	1,000	36,109	419	35,690	553	378	175
	3,000	28,500	92	28,408	177	89	88
	5,000	24,262	9	24,253	0	2	0
	10,000	23,583	5	23,578	0	1	0
	(10 - 1000)	13,109	2,656	10,453	15,107	11,786	3,321
Cyclone cleanout	300	346,749 [a]	35,164	311,585 [s]	88,952 [a]	42,473	46,479
	500	239,365 [a]	2,476	236,889 [s]	1,910	2,086	0
	1,000	176,828 [a]	419	176,409 [s]	315	378	0
	3,000	131,680 [a]	92	131,588 [s]	68	89	0
	5,000	115,569 [a]	9	115,560 [s]	2	2	0
	10,000	113,175 [a]	5	113,170 [s]	0	1	0
	(10 - 1000)	18,235	2,656	15,579	77,000	11,786	65,214
Glovebox cleanout	300	--	35,164	--	228,304 [a]	42,473	185,831 [a]
	500	--	2,476	--	196,134 [a]	2,086	194,048 [a]
	1,000	--	419	--	132,031 [a]	378	131,653 [a]
	3,000	--	92	--	75,128 [a]	89	75,039 [a]
	5,000	--	9	--	40,147	2	40,145
	10,000	--	5	--	19,087	1	19,086
	(10 - 1000)	--	2,656	--	>100,000 [b]	11,786	88,214
Vacuum							
xhaust during cyclone cleanout	300	65,530	35,164	30,366	109,282 [a]	42,473	66,809
	500	3,639	2,476	1,163	4,481	2,086	2,395
	1,000	1,922	419	1,503	787	378	409
	3,000	866	92	774	159	89	70
	5,000	182	9	173	3	2	1
	10,000	112	5	107	1	1	0
	(10 - 1000)	13,094	2,656	10,438	97,000	11,786	85,214

NIOSH Recommendations

Final Report delivered by Dr. Mark Methner - 20 Nov 2008

1. Continue the use of PPE when conducting cleaning/brushdown activities.

2. Use a vacuum unit equipped with a High Efficiency Particulate Air (HEPA) filter to prevent the release of material into the enclosure atmosphere. Ideally, such a vacuum unit would be designed to provide better capture of particulate at the source during cleaning/brushdown activities while retaining explosivity control over the potentially pyrophoric particulate. Ensure that the door to the enclosure remains closed to reduce possible migration of particulate throughout the building.

3. Efforts should be made to keep the material wet when cleaning out the glovebox. In fact, rinsing the glovebox with water may be a better option, provided the rinsate can be collected and disposed of in accordance with ARDEC waste disposal policy.

3. Since the enclosure exhaust ventilation system is outfitted with a HEPA filter, an in-line pressure gauge (e.g. magnahelic®) should be installed upstream and downstream of the filter to monitor the pressure drop across the filter. This type of gauge is routinely used in ventilation systems to monitor filter loading and determine when a filter needs to be changed, based on manufacturer recommendations.

4. “Sticky mats” should be installed inside and outside the door to the enclosure to prevent/reduce nano-scale aluminum powder from being carried out on the footwear of the workers. These mats need to be replaced when the adhesive no longer feels sticky to one’s footwear.

Outcomes

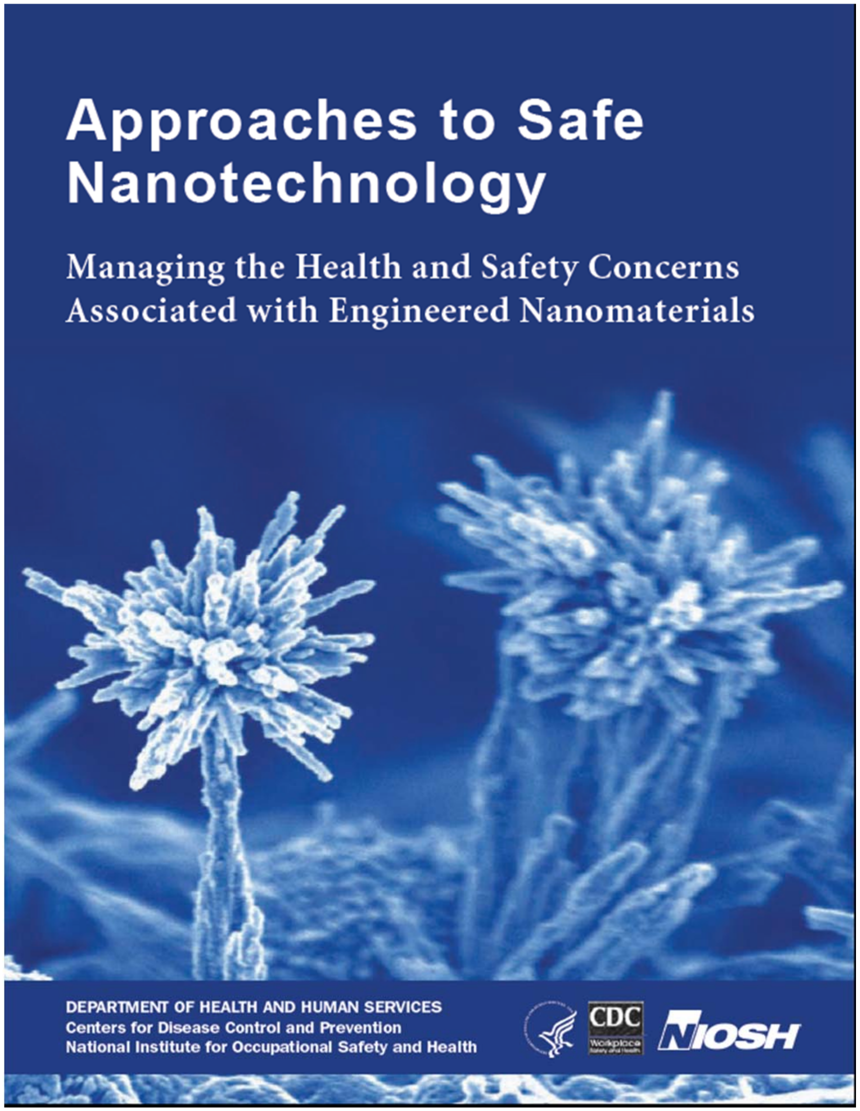


Figure 1. A demonstration of the initial assessment technique with side-by-side sampling using (from left to right) the OPC, co-located open-face filter cassettes, and the CPC: examples of PBZ and source-specific filter-based sampling setup.

pg. 84

Backup Charts

Details of Sampling

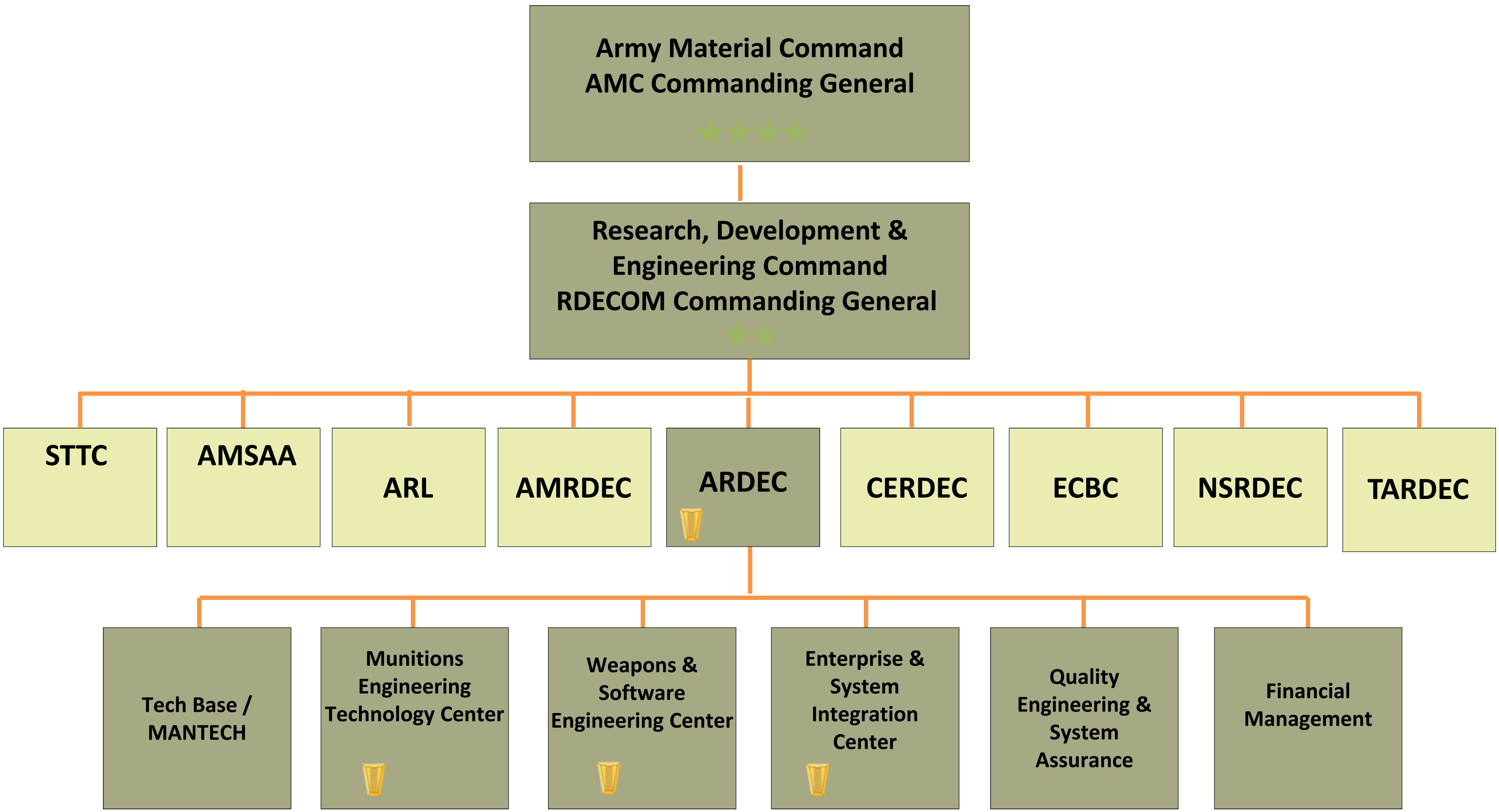
* Adjusted Concentration = Measured Concentration – Average Background Concentration. If Average Background Concentration exceeds the Measured Concentration, the Adjusted Concentration value is considered to be zero. Average Background computed from the average of 3 measurements.

Note: The number concentration of particles in the size ranges (300, 500, 1000, 3,000, 5,000, 10,000 nm) was measured with an ARTI model HHPC-6 optical particle counter and is presented as total number of particles per liter of air (P/liter). The number concentration of particles in the size range (10 nm – 1000 nm) was measured with a TSI Model 3007 condensation particle counter and is presented as total particles per cubic centimeter of air (P/cc).

Note: Missing data indicate operation was not performed.

[a] Concentration exceeds upper limit of HHPC-6 (70,000 p/Liter).
[b] Concentration exceeds upper limit of CPC (100,000 p/cc).

ARDEC Organization – Chain of Command



FE-SEM Microscope